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HELIUM RESEARCH CENTER

INTERNAL REPORT

RECALCULATION OF THE WORK OF Ph. v. JOLLY ON THE DENSITY OF OXYGEN

BY

Robert E. Barieau

BRANCH _____Fundamental Research_____

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HELIUM RESEARCH CENTER

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"Die Veränderlichkeit in der Zusammensetzung der Atmosphärischen
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Wiedemanns Annalen der Physik, Series (2), v. 6, pp. 520-544 (1879).
Abhandlungen der Mathematisch-Physiklischen Classe der Koniglich
Bayerischen Akademie der Wissenschaften, v. 13, Part 2, pp. 51-74
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ABSTRACT

The original data of Ph. v. Jolly on the density of oxygen
has been recalculated, using the latest values of the necessary
physical constants. The value obtained is

$$\rho \;=\; 1.429054 \pm 22 \text{ g/l}$$

$$\text{with } g \;=\; 980.616 \text{ cm/sec}^2.$$

INTRODUCTION

The Helium Research Center is presently engaged in reviewing
and recalculating all of the data that appear in the literature
from which the value of the gas constant R is calculated. In this
report I re-examined the work of Ph. v. Jolly on the determination
of the density of oxygen at one atmosphere and at 0°C.

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    of Mines, Amarillo, Texas.

RECALCULATION OF THE WORK OF Wm. W. JOLLY ON THE DENSITY OF OXYGEN

By

Robert E. Carlson

ABSTRACT

The original data of Wm. W. Jolly on the density of oxygen has been recalculated using the latest values of the necessary physical constants. The value obtained is

$$\rho = 1.429036 \pm 22 \text{ g/l}$$

with $\rho \pm$ 900.016 values.

INTRODUCTION

The Helium Research Center is presently engaged in reviewing and recalculating all of the data that appear in the literature from which the value of the gas constant R is calculated. In this report I re-examined the work of Wm. W. Jolly on the determination of the density of oxygen at one atmosphere and at 0°C.

Ph. v. Jolly determined the density of oxygen by weighing a globe, of about 1 liter capacity, filled with oxygen and then weighing it evacuated. During the filling and evacuation, the globe was completely surrounded by ice and water so that it was accurately at $0°$ C. The globe was evacuated to a pressure of 0.02 mm Hg.

The volume of the globe was determined by weighing the amount of water that would fill the globe at $0°$ C.

Oxygen was prepared by electrolysis. The gas was freed of ozone and hydrogen by passing through a glass tube filled with glass chips and heated to a red heat. The gas was also passed over potassium hydroxide and phosphorous pentoxide.

DETERMINATION OF THE VOLUME OF Ph. v. JOLLY'S GLOBE

Ph. v. Jolly determined the volume of his globe by determining the weight of water that filled the volume. The fact that he corrected the weight of water for the weight of air displaced indicates that the weight of the empty globe must have been determined with the stopcock open to the atmosphere. Under these conditions the relationship for the weight of water in vacuum is given by

$$M_{H_2O} \left(1 - \frac{\rho_2}{\rho_{H_2O}}\right) = M_2 \left(1 - \frac{\rho_2}{\rho_w}\right) - M_1 \frac{\left(1 - \frac{\rho_1}{\rho_w}\right)\left(1 - \frac{\rho_2}{\rho_g}\right)}{\left(1 - \frac{\rho_1}{\rho_g}\right)} \quad (1)$$

In the above equation

M_{H_2O} = mass of water

M_2 = mass of weights on balance when globe filled with water

M_1 = mass of weights on balance when globe filled with air and open to the atmosphere

ρ_1 = density of air during weighing of globe when filled with air

ρ_2 = density of air during weighing of globe when filled with water

ρ_w = density of weights

ρ_g = average density of glass and stopcock in the globe

ρ_{H_2O} = density of water under conditions when the globe was weighed filled with water

$1 - \dfrac{\rho_2}{\rho_{H_2O}}$ is the buoyancy correction factor for the weight of air

displaced by the water. Ph. v. Jolly made this correction. $1 - \dfrac{\rho}{\rho_g}$

is the buoyancy correction factor for the weight of air displaced

by the glass in the globe. As the ratio of two of these quantities

is involved, the ratio only involves the change in the density of

air between the two weighings. This correction is very small and

was neglected by Ph. v. Jolly.

$1 - \dfrac{\rho}{\rho_w}$ is the buoyancy correction factor for the weight of

air displaced by the weights. In his determination of the weight

of water, Ph. v. Jolly applied this correction.

Since Jolly gives the temperature of the air and the baro-
metric pressure, I have recalculated the weight of water applying
all corrections. In these calculations, I have assumed the den-
sity of the glass as being ρ_g = 2.6 g/ml. Ph. v. Jolly gives the
density of his weights as being ρ_w = 8.4 g/ml. I have calculated
the density of air from the equation[2/].

2/ Barieau, Robert E.

   The Density of Moist Air From $0°$ to Near $25°$ C and Near Atmos-

   pheric Pressure. Helium Research Center Internal Report No. 36,

   August 1963.

$$\rho = \rho_o \frac{T_o}{T} P (1 - 0.37807y) \frac{Z_o}{Z} \tag{2}$$

In this equation

   ρ is the density of air in g/liter

   ρ_o is the density of 0.04% CO_2, dry air at $0°$ C and 1 atmos-

   phere pressure

   ρ_o = 1.2932 g/liter

   P is the pressure in atmospheres, where 1 atmosphere is 76 cm

   of Hg at $0°$ C and in a gravitational field of 980.665 cm/sec^2

   in the Potsdam system.

   T is the absolute temperature

   T_o is the absolute temperature of the ice point

   y is the mole fraction of water vapor

Z_o is the compressibility factor of 0.04% CO_2, dry air at

0° C and 1 atmosphere

Z is the compressibility factor of the gas at P and T

$$\frac{Z_o}{Z} = 1 - 0.000602 (P - 1) + (0.00254y + 0.0758y^2)P$$
$$- (0.0000105 + 0.0000131y + 0.00131y^2)tP \tag{3}$$

where in this equation, t is the temperature in °C.

The mole fraction of water in air saturated with water vapor

was taken as (3)

(3) Reference (2) page 17

$$y_{sat} = 1.0042 \frac{P_s}{P} \tag{4}$$

where P_s is the vapor pressure of pure water in atmospheres and P

is the total atmospheric pressure in atmospheres. The vapor pres-

sure of water was calculated from the equation given by Osborne,

Stimson, and Ginnings (4)

(4) Osborne, N. S., H. F. Stimson, and D. C. Ginnings. Thermal

Properties of Saturated Water and Steam. J. Research NBS,

v. 23, 1939, pp. 261-270.

Z_a is the compressibility factor of 0.03% CO_2, dry air at 0° C and 1 atmosphere

Z is the compressibility factor of the gas at P and T

$$\frac{PV}{Z} = 1 - 0.00507 (Z - 1) + (0.00234y + 0.0194y^2)t \\ - (0.000055 + 0.000013y + 0.00131y^2)t^2 \quad (2)$$

where in this equation, t is the temperature in °C.

The mole fraction of water in air saturated with water vapor was taken as (3)

(3) Reference (2) page 11

$$x_{sat} = 1.0042 \frac{P_w}{P} \quad (4)$$

where P_w is the vapor pressure of pure water in atmospheres and P is the total atmospheric pressure in atmospheres. The vapor pressure of water was calculated from the equation given by Osborne, Stimson, and Ginnings (4).

(4) Osborne, N.S., H.F. Stimson, and D.C. Ginnings, "Thermal Properties of Saturated Water and Steam," J. Research NBS, v.23, 1939, pp. 261-270.

$$\log_{10} P_{atm} = -3.142305 \left[\frac{10^3}{T} - \frac{10^3}{373.16} \right]$$

$$+ 8.2 \log_{10} \frac{373.16}{T} \tag{5}$$

$$- 0.0024804 (373.16 - T)$$

The density of liquid water was taken from the table of Tilton and Taylor (5)

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(5) Tilton, L. W., and J. K. Taylor. Accurate Representation of the Refractivity and Density of Distilled Water as a Function of Temperature. J. Research NBS, v. 18, 1937, pp. 205-214.

Ph. v. Jolly weighed his globe filled with air, with the stop-cock open to the atmosphere, first on the right pan of his balance and then on the left pan. The two values were 142.074331 g and 142.072500 g with a geometric mean of 142.073415 g. Jolly adds to this 0.001876 as the sum of the corrections to his individual weights, giving

$$M_1 = 142.075291 \text{ g}$$

Atmospheric conditions during this weighing were $t = 7.1^\circ$ C, $P = 721.57$ mm Hg at 0° C under local gravity. In correcting the atmospheric pressure to standard gravity, I used $g_{local} = 980.7361$ cm/sec^2 and $g_{standard} = 980.665$ cm/sec^2.

Then $P = \dfrac{721.57 \times 980.7361}{760 \times 980.665}$

$P = 0.949503$ atmospheres.

Using the equations given previously, I calculate for the vapor pressure of liquid water at $7.1°$ C.

$P_s = 0.0099495$ atmospheres.

Then y_{sat} $(7.1°$ C$) = 1.0042 \times \dfrac{0.0099495}{0.949503}$

or $y_{sat} = 0.0105226$

Jolly does not give a hygrometer reading for this weighing, but he does give a value of 65% for the weighing when water was present in the globe. I will take a relative humidity of 65% for the first weighing also. I then calculate for the density of air

$\rho_1 = 0.0011937$ g/ml

Then the true mass of the globe is

$$\dfrac{M_1 \left(1 - \dfrac{\rho_1}{\rho_w}\right)}{\left(1 - \dfrac{\rho_1}{\rho_g}\right)} = 142.075291 \; \dfrac{\left(1 - \dfrac{.0011937}{8.4}\right)}{\left(1 - \dfrac{.0011937}{2.6}\right)}$$

$$= 142.075291 \times \dfrac{0.9998578929}{0.9995408846}$$

$$= 142.120351 \text{ g}$$

Then $F = \dfrac{731.57 \times 980.7381}{780 \times 980.665}$

$P = 0.94503$ atmospheres.

Using the equations given previously, I calculate for the vapor pressure of liquid water at 7.7° C.

$F_s = 0.0098491$ atmospheres.

Then Y_{sat} $(7.7^\circ$ C$) = 1.0042 \times \dfrac{0.0098491}{0.94503}$

or Y_{sat} $= 0.010532$?

Jolly does not give a hygrometer reading for this weighing, but he does give a value of 65% for the weighing when water was present in the globe. I will take a relative humidity of 65% for the first weighing also. I then calculate for the density of air

$\rho_1 = 0.0011937$ g/ml

Then the true mass of the globe is

$$142.071931 \times \dfrac{(1 - \dfrac{\rho_2}{M_{2.2}})}{(1 - \dfrac{\rho_1}{M_{2.2}})} = 142.071931 \times \dfrac{(1 - \dfrac{.0011937}{2.2})}{(1 - \dfrac{.0011937}{2.2})}$$

$= 142.071931 \times \dfrac{0.99945?049?}{0.99945?06?6}$

$= 142.120931$ g

and with a density of 2.6 the glass occupies 54.7 ml.

When filled with water at $0°$ C, the globe and water weighed 1150.304760 g on the left pan and 1150.292000 on the right pan giving a geometrical mean of 1150.298380. To this, Jolly adds 0.001302 for the calibration of his weights to give

$$M_2 \ = \ 1150.299682 \text{ g.}$$

During this weighing, atmospheric conditions were $t = 6.4°$ C, $P = 721.3$ mm Hg $0°$ C (local gravity), hygrometer $= 65\%$. I calculate

$$P \ = \ \frac{721.3}{760} \ \times \ \frac{980.7361}{980.665}$$

$$P \ = \ 0.949148 \text{ atmospheres.}$$

Using the equations given previously, I calculate for the vapor pressure of liquid water at $6.4°$ C

$$P_s \ = \ 0.0094821 \text{ atmospheres.}$$

Then

$$y(\text{sat}) \ (6.4° \text{ C}) \ = \ 1.0042 \times \frac{0.0094821}{0.949148}$$

or

$$y(\text{sat}) \ = \ 0.0100321$$

and with the air 65% saturated with respect to water vapor, the mole fraction of water vapor then is

$$y = .65 \times .0100321 = 0.00652087.$$

Then with $t = 6.4°$ C, $P = 0.949148$ atmospheres and $y = 0.00652087$, I calculate for the density of air

$$\rho_2 = 0.0011964 \text{ g/ml}.$$

Tilton and Taylor (6)

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(6) Reference 5, page 213

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give for the density of water at $6.4°$ C

$$\rho_w = 0.9999546 \text{ g/ml}$$

Then the expression for the mass of water, M_{H_2O}, is given by

$$M_{H_2O} (1 - \frac{0.0011964}{0.9999546}) = 1150.299682 (1 - \frac{0.0011964}{8.4})$$

$$-142.075291 \frac{(1 - \frac{.0011937}{8.4})(1 - \frac{.0011964}{2.6})}{(1 - \frac{.0011937}{2.6})}$$

and with the air 65% saturated with respect to water vapor, the

mole fraction of water vapor then is

$$y = .65 \times .010321 = 0.0067209)$$

Then with $t = 6.0°$ C., $P = 0.945168$ atmospheres and

$y = 0.0067208)$, I calculate for the density of air

$$\rho_2 = 0.001186 \text{ g/ml}$$

Tilton and Taylor (6)

(d) Reference 5, page 213

give for the density of water at 6.0° C

$$\rho_w = 0.9999350 \text{ g/ml}$$

Then the expression for the mass of water, M_{H_2O}, is given by

$$M_{H_2O} (1 - 0.999350) = 1110.299481 (1 - \frac{0.001186}{2.5})$$

$$-161.073281 \frac{(1 - \frac{0.001197}{2.5})(1 - \frac{0.001186}{2.5})}{(1 - \frac{0.001197}{2.5})}$$

or

$$M_{H_2O} \times 0.9988035457 = 1150.299682 \times .9998575714$$

$$- 142.075291 \times \frac{0.9998578929}{0.9995408846} \times 0.9995398462$$

$$= 1150.135846 - 142.054953 = 1008.080893$$

Then M_{H_2O} = 1009.288461 g.

Jolly calculated

$$M_{H_2O} = 1009.286871$$

which differs by 1.5 ppm from the value I have calculated.

Taking the density of water (7)

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(7) Reference 5, page 213

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at 0° C as 0.9998676 g/ml, I calculate for the volume of Jolly's

globe at 0° C

$$V = \frac{1009.288461}{0.9998676}$$

$$V = 1009.4221 \text{ ml}$$

or

$$V = 1.0094221 \text{ liters}$$

DETERMINATION OF THE MASS OF OXYGEN

Jolly determined the mass of oxygen in the following way. He completely surrounded the globe with ice and water and admitted oxygen until the globe was filled at atmospheric pressure. After equilibrium, the barometer was read and the stopcock closed. The globe was then removed and weighed. The globe was then returned to the ice bath and evacuated to 0.02 mm of Hg, the stopcock closed and the evacuated globe was weighed.

The weighings were carried out in the following way. Jolly had a tare globe that had the same external volume as his oxygen weighing globe, to within 0.06 ml. His weighing globe and tare globe were placed on the opposite pans of the balance. When his weighing globe was filled with oxygen, weights were necessary on the pan with the tare globe. When the weighing globe was evacuated, weights were necessary on the pan with the weighing globe. To correct for inequality of the balance arms, each weighing was done twice, interchanging the objects on the balance pans. Jolly applied corrections for the difference between the nominal value and actual value of his weights.

Let M_T be the mass of the tare globe and its contents

Let M_G be the mass of the globe to be filled with oxygen

Let V_T be the external volume of the tare globe during the weighing

Let V_G be the external volume at the time of weighing of the globe to be filled with oxygen

Let ρ_{air} be the density of the air at time of weighing

Let ρ_w be the density of the weights

Let M_w be the mass of weights that bring the balance to

equilibrium and

Let g be the mass of oxygen in the main globe.

Let the first weighing be with the main globe filled with oxygen.

When the balance is in equilibrium the following equation applies.

$$M_G + g_1 - V_{G_1} \rho_{air_1} = M_T - V_{T_1} \rho_{air_1} + M_{w_1}(1 - \frac{\rho_{air_1}}{\rho_w}) \quad (6)$$

Let the second weighing be when the main globe is evacuated. Then

at equilibrium

$$M_G + g_2 - V_{G_2} \rho_{air_2} + M_{w_2}(1 - \frac{\rho_{air_2}}{\rho_w}) = M_T - V_{T_2} \rho_{air_2} \quad (7)$$

Then

$$g_1 - g_2 = M_{w_1}(1 - \frac{\rho_{air_1}}{\rho_w}) + M_{w_2}(1 - \frac{\rho_{air_2}}{\rho_w})$$

$$\quad (8)$$

$$+ (V_{G_1} - V_{T_1}) \rho_{air_1} - (V_{G_2} - V_{T_2}) \rho_{air_2}$$

This equation includes all buoyancy corrections.

Jolly did not give the temperature, pressure, and relative

humidity of the air during any of his weighings. We can only

assume a constant value for the density of air.

V_T and V_G will be a function of the temperature and also a function of the pressure difference between the inside and outside of the globe.

I assume this variation may be expressed by

$$V_T = (V_o + \delta)(1 + \alpha t) \tag{9}$$

$$V_G = V_o (1 + \alpha t)(1 + \beta \Delta P) \tag{10}$$

where ΔP is the pressure difference between inside and outside.

Then

$$V_G - V_T = V_o (1 + \alpha t) \beta \Delta P - \delta (1 + \alpha t) \tag{11}$$

For the first weighing, we assume $\Delta P = 0$.

Then

$$g_1 - g_2 = (M_{w_1} + M_{w_2})(1 - \frac{\rho_{air}}{\rho_w})$$

$$\tag{12}$$

$$- V_o (1 + \alpha t_2) \beta \Delta P_2 \rho_{air}$$

where

$$\Delta P_2 = P_{inside} - P_{outside} \tag{13}$$

during the time of the weighing when the main globe is evacuated.

The correction term $V_o (1 + \alpha t_2) \beta \Delta P_2 \rho_{air}$ has been called the correction for the contraction of the globe. Jolly neglected this correction. The necessity for making this correction was first

V_T and V_G will be a function of the temperature and also a function of the pressure difference between the inside and out- side of the globe.

I assume this variation may be expressed by

$$V_T = V_0 (1 + A)(1 + \alpha t) \tag{9}$$

$$V_G = V_0 (1 + \alpha t)(1 + B\Delta P) \tag{10}$$

where ΔP is the pressure difference between inside and outside.

Then

$$V_G - V_T = V_0 (1 + \alpha t) B\Delta P - A(1 + \alpha t) \tag{11}$$

For the first weighing, we assume $\Delta P = 0$.

Then

$$E_1 - E_2 = (K_1 + K_2)(1 - \frac{d_{air}}{d}) \tag{12}$$

$$- V_0 (1 + \alpha t) B\Delta P \cdot d_{air}$$

where

$$\Delta P = P_{inside} - P_{outside} \tag{13}$$

during the time of the weighing when the main globe is evacuated. The correction term $V_0 (1 + \alpha t) B\Delta P \cdot d_{air}$ has been called the correction for the contraction of the globe. Jolly neglected this correction. The necessity for making this correction was first

pointed out by Lord Rayleigh (8)(9)

(8) Lord Rayleigh. On the Relative Densities of Hydrogen and Oxy-

gen. Preliminary Notice. Proc. Roy. Soc. (London), v. 43,

1888, pp. 356-363.

(9) Lord Rayleigh. On the Relative Densities of Hydrogen and Oxy-

gen. Preliminary Notice. The Chemical News, v. 57, 1888,

pp. 73-75.

The factor $(1 - \dfrac{\rho_{air}}{\rho_w})$ is the correction for air buoyancy on

the weights. Ph. v. Jolly seems to have neglected this correction

in determining the weight of his gases; while he, as we have seen,

applied a buoyancy correction to his weights in determining the

weight of water that filled his globe at 0° C. In regard to this

point Lord Rayleigh says (10)

(10) Lord Rayleigh. II On the Densities of the Principal Gases.

Proc. Roy. Soc. (London), v. LIII, 1893, pp. 134-149. Footnote

on page 140.

"In v. Jolly's calculations the buoyancy of the weights seems

to be allowed for in dealing with the water, and neglected in

dealing with the gases. If this be so, the result would be affected

with a slight error which, however, far exceeds any that could arise

pointed out by Lord Rayleigh (8)(9).

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(9) Lord Rayleigh. On the Relative Densities of Hydrogen and Oxy-
gen. Preliminary Notice. The Chemical News, v. 57, 1888,
pp. 73-75.

The factor $(1 - \frac{\Delta a_1}{P_w})$ is the correction for air buoyancy on
the weights. Ph. v. Jolly seems to have neglected this correction
in determining the weight of his gases, while he, as we have seen,
applied a buoyancy correction to his weights in determining the
weight of water that filled his globe at 0° C. In regard to this
point Lord Rayleigh says (10)

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Proc. Roy. Soc. (London), v. LIII, 1893, pp. 134-149. Footnote
on page 140.

"In v. Jolly's calculations the buoyancy of the weights seems
to be allowed for in dealing with the water, and neglected in
dealing with the gases. If this be so, the result would be affected
with a slight error which, however, far exceeds any that could arise

from neglecting buoyancy altogether." Lord Rayleigh evidently

overlooked the fact that in weighing his water, Jolly used gold

plated brass weights, while in weighing his gases, he used plati-

num weights. Under these conditions, neglecting buoyancy alto-

gether introduces an error of 87 ppm low in the density of oxygen,

while applying the buoyancy correction to the water determination

and neglecting it in the determination of weight of gas, intro-

duces an error of 56 ppm high in the density of oxygen. Applying

both buoyancy corrections and assuming a 10% uncertainty in the

density of air during the gas weight determinations, reduces the

uncertainty in the density of oxygen to 5 ppm. I have therefore

applied a buoyancy correction for the weights in the determination

of the mass of oxygen. In these calculations, I have taken the

density of air as being 0.0012 g/ml.

I reproduce below the data on the weight of oxygen given by

Jolly in his paper.

TABLE 1. - Original data published by Jolly

	Gew. d. Kolbens 0°		Kolben 0° 0.02 mm	Gew. d. 0 0°		Gew. d.0 0° 760 mm
	Bar.	K = T+	K = T-	Bar.	Gew.	
I	714.45	0.083799	1.272183	714.43	1.355982	1.442470
II	711.30	0.077913	1.272187	711.28	1.350100	1.442579
III	715.02	0.074904	1.272180	715.00	1.347084	1.442489
IV	720.42	0.095182	1.272224	720.40	1.367406	1.442570
V	722.02	0.098103	1.272380	722.000	1.370483	1.442571
VI	706.93	0.069659	1.272188	706.91	1.341847	1.442562
VII	693.79	0.044552	1.272222	693.77	1.316774	1.442478
					Mittel	1.442545

The second column, headed Bar., is evidently the barometric pressure reduced to mm of Hg at $0°$ C under local gravity conditions. The third column gives the weight that must be added to the tare to balance the globe filled with oxygen to a pressure equal to the barometric pressure. The fourth column gives the weights that must be added to the evacuated globe to balance the tare. These are the data that I have called M_{w_1} and M_{w_2}.

Evidently, column 6 is nothing but the sum of columns 3 and 4, that is $M_{w_1} + M_{w_2}$.

The fifth column is the barometric pressure minus 0.02 mm, which was the pressure when the globe was evacuated.

Column seven is evidently column six times 760, divided by the pressure listed in column five. In table 2, I give this number calculated from columns five and six and compare it with Jolly's value given in column seven.

TABLE 2. - Comparison of calculated data

	ΔP	$M_{w_1} + M_{w_2}$	$(M_{w_1} + M_{w_2}) \frac{760}{\Delta P}$	Jolly	Δ
I	714.43	1.355982	1.442473	1.442470	+.000003
II	711.28	1.350100	1.442577	1.442579	-.000002
III	715.00	1.347084	1.431866	1.442489	-.010623
IV	720.40	1.367406	1.442572	1.442570	+.000002
V	722.00	1.370483	1.442614	1.442571	+.000043
VI	706.91	1.341847	1.442622	1.442562	+.000060
VII	693.77	1.316774	1.442478	1.442478	.000000

Evidently there is a typographical error in connection with experiment III and possibly with experiments V and VI.

If $M_{w_1} + M_{w_2} = 1.357084$ for experiment III, then

$$\frac{(M_{w_1} + M_{w_2})760}{715.00} = 1.442495.$$

This is to be compared with Jolly's tabulated value of 1.442489.

This is sufficiently close to my calculated value that for experi-

ment III, I take $M_{w_1} = 0.084904$.

I then find the values given in table 3.

TABLE 3. - Accepted values of $M_{w_1} + M_{w_2}$

	$M_{w_1} + M_{w_2}$	$(M_{w_1} + M_{w_2}) \dfrac{760}{\Delta P}$	Jolly
I	1.355982	1.442473	1.442470
II	1.350100	1.442577	1.442579
III	1.357084	1.442495	1.442489
IV	1.367406	1.442572	1.442570
V	1.370483	1.442614	1.442571
VI	1.341847	1.442622	1.442562
VII	1.316774	1.442478	1.442478
Mean		1.4425473	1.4425313

At the bottom of table 3, I give the mean of the values calcu-

lated by me and the mean of the values tabulated by Jolly. However,

Jolly gives the mean of the values tabulated by him as 1.442545.

This essentially agrees with the mean of my calculated values and

not with the mean of his tabulated values. I have therefore con-

cluded that the values given in column 2 in table 3 are the values to

If $M_{w_1} + M_{w_2} = 1.357084$ for experiment III, then

$$\frac{(M_{w_1} + M_{w_2})760}{715.00} = 1.642695.$$

This is to be compared with Jolly's tabulated value of 1.642485.

This is sufficiently close to my calculated value that for experiment III, I take $M_{w_1} = 0.084904.$

I then find the values given in table 3.

TABLE 3. – Accepted values of $M_{w_1} + M_{w_2}$

	$M_{w_1} + M_{w_2}$	$(M_{w_1} + M_{w_2})\frac{760}{DF}$	Jolly
I	1.355982	1.642673	1.642670
II	1.350100	1.642577	1.642576
III	1.357084	1.642695	1.642495
IV	1.367404	1.642572	1.642570
V	1.370483	1.642614	1.642571
VI	1.341847	1.642622	1.642562
VII	1.316774	1.642628	1.642678
Mean		1.642673	1.642513

At the bottom of table 3, I give the mean of the values calcu-
lated by me and the mean of the values tabulated by Jolly. However,
Jolly gives the mean of the values tabulated by him as 1.642545.
This essentially agrees with the mean of my calculated values and
not with the mean of his tabulated values. I have therefore con-
cluded that the values given in column 2 in table 3 are the values to

be used in calculating the weight of oxygen, $g_1 - g_2$ of equation (12). These values must be corrected for the air buoyancy on the platinum weights and for the contraction of the globe.

For the buoyancy correction, I have taken the density of air as 0.0012 g/ml and the density of platinum as 21.45 g/ml. The factor

$$1 - \frac{\rho_{air}}{\rho_w} = 1 - \frac{0.0012}{21.45}$$

$$= 0.99994406$$

must be multiplied by each of the values of $(M_{w_1} + M_{w_2})$ listed in table 3.

In order to make the correction for the contraction of the globe, it is necessary to know the value of β, used in equations (10) and (12). This coefficient has been determined by Moles and Miravalles (11) (12),

(11) Moles, E. and R. Miravalles
      A Cerca de la Compresibilidad de los Matraces vacios en la
      Determination de gases (The Compressibility of Evacuated
      Flasks in the Determination of Gas Densities) Anales de la
      Sociedad Espanola de fisica y quimica, v. 20, 1922, pp. 104-
      116.

(12) Moles, E. and R. Miravalles

Sur la Contraction des Ballons Vides dans les Mesures de la

Densite de Gas (On the Contraction of Empty Flasks in Measure-

ment of gas Densities)   J. de Chemie Physique, v. 21, 1924,

pp. 1-9.

who made measurements on many different globes. They give

$$\beta (atm^{-1}) = \frac{V}{w} \times 15.5 \times 10^{-6} \qquad (14)$$

where V is the volume of the flask in ml and

w is the weight of the flask in grams

For Jolly's flask

    V = 1009.42 ml

    w = 142.12 gm

   V/w = 7.103

So that

$$\beta = 1.101 \times 10^{-4} (atm^{-1})$$

Since this correction is a small correction, I have taken

$V_o (1 + \alpha t_2)$ in equation (12) as being

$$V_o(1 + \alpha t_2) = 1009.4 + 54.7$$

$$= 1064.1 \text{ ml.}$$

(12) Moles, E., and E. Miravalles

Sur la Contraction des Ballons Vides dans les Mesures de la

Densité de Gas (On the Contraction of Empty Flasks in Measure-

ment of gas Densities)   J. de Chemie Physique; v. 21, 1924,

pp. 1-9.

who made measurements on many different globes. They give

$$\beta(atm^{-1}) \; = \; \frac{w}{V} \times 13.5 \times 10^{-6} \qquad (14)$$

where V is the volume of the flask in ml and

w is the weight of the flask in grams

For Jolly's flask

V = 1005.42 ml

w = 142.12 gm

V/w = 7.103

So that:

$$\beta \; = \; 1.101 \times 10^{-4} \; (atm^{-1})$$

Since this correction is a small correction, I have taken

$V_0(1 + \sigma e_2)$ in equation (12) as being

$$V(1 + \sigma e_2) \; = \; 1005.4 + 34.7$$

$$= \; 1004.1 \; ml.$$

54.7 is the volume occupied by the glass in the flask. I have

taken ΔP_2 in equation (12) as being minus the pressure given in

column 2 of table 2, divided by 760.

The calculations of the weights of oxygen are summarized in

table 4. $g_1 - g_2$ was calculated using equation (12).

TABLE 4. - Calculation of mass of oxygen

	$(M_{w_1} + M_{w_2})(1 - \frac{\rho_{air}}{\rho_w})$	$-V_o(1 + \alpha t_2)\beta \Delta P_2 \rho_{air}$	$g_1 - g_2$
I	1.355906	0.000132	1.356038
II	1.350024	0.000132	1.350156
III	1.357008	0.000132	1.357140
IV	1.367330	0.000133	1.367463
V	1.370406	0.000134	1.370540
VI	1.341772	0.000131	1.341903
VII	1.316700	0.000128	1.316828

The values of the correction for the contraction of the globe,

represent a correction of 0.00014 in the final value of the density

of oxygen. Lord Rayleigh (13)

(13) Reference 10, page 147

estimated this correction to be 0.00032, while Moles (14)

(14) Moles, E.

Etude Critique des Valuers Modernes de la Densite du gaz

Oxygene (Critical Study of Modern Values of the Density of

Oxygen Gas) Journal de Chimie Physique et Revue Generale des

Colloides, v. 19, 1921, pp. 100-120.

estimated it to be 0.00020, which in a later paper by Moles and

Gonzalez (15),

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(15)   Moles, E. and F. Gonzalez

Nouvelle Revision de la Densite Normale du Gaz Oxygene.   (New

Revision of the Normal Density of Oxygen Gas.)   Journal de

Chimie Physique, v. 19, 1921, pp. 310-323.   Footnote 2 on

page 322.

---

was changed to 0.00016.

CALCULATION OF THE DENSITY OF OXYGEN

In this section I derive the formula necessary to calculate the

density of oxygen at 0° C and at 1 atmosphere where in this section,

1 atmosphere is defined as 760 mm of Hg at 0° C under the conditions

of local gravity.

In each experiment, the globe contained g_1 grams of oxygen at

a pressure P_1, near 1 atmosphere and at a volume V_o. When evacuated

to the pressure P_2, the globe contained g_2 grams of oxygen, in the

volume V_2 where

$$V_2 = V_o [1 + \beta (P_2 - P_1)] \tag{15}$$

I apply the exact equations

$$P_1 V_o = \frac{g_1 RT_o Z_1}{M} \tag{16}$$

estimated it to be 0.00020, which in a later paper by Moles and

Gonzales (15).

(15) Moles, E. and F. Gonzalez

Nouvelle Revision de la Densite Normale du Gaz Oxygène. (New

Revision of the Normal Density of Oxygen Gas.) Journal de

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In each experiment, the globe contained g_1 grams of oxygen at

a pressure P_1, near 1 atmosphere and at a volume V_o. When evacuated

to the pressure P_2, the globe contained g_2 grams of oxygen, in the

volume V_2 where

$$V_2 = V_o [1 + \beta (P_2 - P_1)]$$ (15)

I apply the exact equations.

$$P_1 V_o = \frac{g_1 RT Z}{M}$$ (16)

$$P_2 V_2 = \frac{g_2}{M} RT_o Z_2 = P_2 V_o [1 + \beta(P_2 - P_1)] \tag{17}$$

where M is the molecular weight of oxygen and Z is the compressibility factor. Then

$$\frac{P_1}{P_2} = \frac{g_1}{g_2} \frac{Z_1}{Z_2} [1 + \beta(P_2 - P_1)] \tag{18}$$

or finally

$$g_2 = g_1 \frac{Z_1}{Z_2} \frac{P_2}{P_1} [1 + \beta(P_2 - P_1)] \tag{19}$$

Thus

$$g_1 - g_2 = g_1 \left(1 - \frac{Z_1}{Z_2} \frac{P_2}{P_1} [1 + \beta(P_2 - P_1)] \right) \tag{20}$$

and

$$g_1 = \frac{g_1 - g_2}{1 - \frac{Z_1}{Z_2} \frac{P_2}{P_1} [1 + \beta(P_2 - P_1)]} \tag{21}$$

Now let g_{760} be the grams of oxygen that would be in the globe at a pressure of 760 mm of Hg at 0° C and with the barometric pressure the same. With P_{760} representing this pressure, we have

$$\frac{P_1}{P_{760}} = \frac{g_1}{g_{760}} \frac{Z_1}{Z_{760}} \tag{22}$$

$$P_2 V_2 = \frac{M}{R T_2 Z_2} = P_2 V_o [1 + \beta(T_2 - P_1)] \tag{17}$$

where M is the molecular weight of oxygen and Z is the compressi-
bility factor. Then

$$\frac{P_2}{P_1} = \frac{g_2 Z_2}{g_1 Z_1} [1 + \beta(T_2 - P_1)] \tag{18}$$

or

Thus

$$g_2 = g_1 \frac{Z_1}{Z_2} \frac{P_2}{P_1} [1 + \beta(T_2 - P_1)] \tag{19}$$

$$g_1 - g_2 = g_1 \left(1 - \frac{Z_1}{Z_2} \frac{P_2}{P_1} [1 + \beta(T_2 - P_1)] \right) \tag{20}$$

and

$$g_1 = \frac{g_1 - g_2}{1 - \frac{Z_1}{Z_2} \frac{P_2}{P_1} [1 + \beta(T_2 - P_1)]} \tag{21}$$

Now let g_{760} be the grams of oxygen that would be in the globe
at a pressure of 760 mm of Hg at 0° C and with the barometric pres-
sure the same. With P_{760} representing this pressure, we have

$$\frac{P_2}{P_{760}} = \frac{g_1}{g_{760}} \frac{Z_1}{Z_2} \tag{22}$$

$$g_{760} = g_1 \frac{Z_1}{Z_{760}} \frac{P_{760}}{P_1} \tag{23}$$

and substituting for g_1 from equation (21), we have

$$g_{760} = \frac{(g_1 - g_2) \dfrac{Z_1}{Z_{760}} \dfrac{P_{760}}{P_1}}{1 - \dfrac{Z_1}{Z_2} \dfrac{P_2}{P_1} [1 + \beta(P_2 - P_1)]} \tag{24}$$

and finally

$$g_{760} = \frac{(g_1 - g_2) P_{760}}{P_1 - \dfrac{Z_1}{Z_2} P_2 [1 + \beta(P_2 - P_1)]} \frac{Z_1}{Z_{760}} \tag{25}$$

Equation (25) allows the mass of oxygen, that would fill Jolly's

globe at a pressure of 760 mm Hg at 0° C, to be calculated.

Jolly assumed all of the compressibility factors were equal

to one. For making the compressibility correction, I have assumed

the compressibility factor, at 0° C to be given by

$$Z = 1 - 0.000965 \frac{P_{mm}}{760} \tag{26}$$

With the pressure in mm of Hg at 0° C, β is given by

$$\beta = \frac{0.0001101}{760} = 1.45 \times 10^{-7} (\text{mm Hg})^{-1}.$$

$$M_{760} = g_i^1 \frac{T_1}{760} \frac{g^2}{g^1} T_{760} \tag{23}$$

and substituting for g_i^1 from equation (21), we have

$$g_{760} = \frac{(g_1 - g_2^1) \frac{T_1}{760} \frac{T^2}{760}}{1 - \frac{g^2}{g_1^1} \frac{T_1}{g} [1 + B(P_2 - P_1)]} \tag{24}$$

and finally

$$M_{760} = \frac{(g_1 - g_2^1) T_{760}^2 \frac{T_1}{g}}{1 - \frac{T_1}{g^2} \frac{T_2}{g_1^1} [1 + B(P_2 - P_1)]} \frac{T_1}{760} \tag{25}$$

Equation (25) allows the mass of oxygen, that would fill Jolly's globe at a pressure of 760 mm Hg at 0° C, to be calculated. Jolly assumed all of the compressibility factors were equal to one. For making the compressibility correction, I have assumed the compressibility factor, at 0° C to be given by

$$z = 1 - 0.00065 \frac{P}{760} \tag{26}$$

With the pressure in mm of Hg at 0° C, B is given by

$$B = \frac{0.000101}{760} = 1.45 \times 10^{-7} \ (mm \ Hg)^{-1}$$

The details of the calculations of g_{760} are summarized in table 5.

TABLE 5. - <u>Calculation of mass of oxygen needed to fill Jolly's globe at 0° C and 760 mm of Hg at local gravity</u>

	P_1	$g_1 - g_2$	Z_1/Z_{760}	g_{760}
I	714.45	1.356038	1.0000579	1.4426165
II	711.30	1.350156	1.0000619	1.4427259
III	715.02	1.357140	1.0000572	1.4426369
IV	720.42	1.367463	1.0000503	1.4427042
V	722.02	1.370540	1.0000482	1.4427432
VI	706.93	1.341903	1.0000675	1.4427793
VII	693.79	1.316828	1.0000842	1.4426590
			Mean	1.4426950 g

The mean for g_{760} given by Jolly is 1.442545 which means my calculated value is higher by a factor 1.00010. This is principally due to the neglect, by Jolly, of the compressibility factor, Z/Z_{760}, and the contraction of the globe.

Using a value of 1.0094221 liters for the volume of Jolly's globe, the values of the density of oxygen at 0° C and under a pressure of 760 mm Hg at 0° C and local gravity were calculated. These values are given in table 6.

TABLE 6. - <u>Density of oxygen at 0° C, 760 mm of Hg, local gravity</u>

	ρ, g/l
I	1.4291509
II	1.4292593
III	1.4291711
IV	1.4292378
V	1.4292764
VI	1.4293122
VII	1.4291930
Mean	1.429229 $\pm$ 22

The details of the calculations of s_{760} are summarized in table 5.

TABLE 5. - Calculation of mass of oxygen needed to fill Jolly's globe at 0°C and 760 mm of Hg at local gravity

	F_i	$s_i - s_g$	z_i^2/z_{760}	s_{760}
I	714.45	1.355638	1.0000579	1.4426185
II	711.30	1.350156	1.0000619	1.4427259
III	715.02	1.357140	1.0000572	1.4426369
IV	730.42	1.367463	1.0000503	1.4427042
V	732.02	1.370540	1.0000582	1.4427837
VI	706.93	1.341903	1.0000575	1.4427993
VII	693.79	1.315828	1.0000842	1.4425894
Mean				1.4426930 g

The mean for s_{760} given by Jolly is 1.442545 which means my calculated value is higher by a factor 1.00010. This is principally due to the neglect, by Jolly, of the compressibility factor, $z_i^2/760$, and the contraction of the globe.

Using a value of 1.0054221 liters for the volume of Jolly's globe, the values of the density of oxygen at 0°C and under a pressure of 760 mm Hg at 0°C and local gravity were calculated. These values are given in table 6.

TABLE 6. - Density of oxygen at 0°C, 760 mm of Hg, local gravity

	s_i, g/l
I	1.4291509
II	1.4292593
III	1.4291711
IV	1.4292372
V	1.4292764
VI	1.4291722
VII	1.4291930
Mean	1.4292179 ± 22

The plus or minus is the standard deviation of the mean.

REDUCTION OF THE DENSITY OF OXYGEN TO GRAVITY OF 980.616 CM/SEC^2

Ph. v. Jolly gives for his laboratory in Munich,

$$\text{latitude} = 48°\,8'$$

$$\text{elevation} = 515 \text{ meters}$$

Woollard and Rose (16)

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(16) Woollard, George P. and John C. Rose

International Gravity Measurements. Published by Society of

Exploration Geophysicists, October 1963, 518pp., Composed and

Printed by George Banta Company, Inc. Menasha, Wisconsin,

p. 514.

---

give for the acceleration of gravity, at Munich, in the Potsdam

system for the Residenz station

$$g = 980.7384 \text{ cm/sec}^2$$

with

$$\text{latitude} = 48°\,8.5'\text{N}$$

$$\text{longitude} = 11°\,34.9'\text{ E}$$

$$\text{elevation} = 510 \text{ meters}$$

The change in g from a latitude of $48°\,8.5'$ to $48°\,8'$ is

The plus or minus is the standard deviation of the mean.

REDUCTION OF THE DENSITY OF OXYGEN TO GRAVITY OF 980.616 CM/SEC^2

Ph. v. Jolly gives for his laboratory in Munich,

latitude = 48°8'.

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Printed by George Banta Company, Inc. Menasha, Wisconsin,

p. 516.

---

give for the acceleration of gravity, at Munich, in the Potsdam

system for the Residual station

$g = 980.7384$ cm/sec^2

with

latitude = 48° 8.5'N

longitude = 11° 36.5' E

elevation = 510 meters

The change in g from a latitude of 48° 8.5' to 48° 8' is

given by Lambert and Darling's tables (17)

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(17) Lambert, W. D., and F. W. Darling

Tables for Theoretical Gravity According to the New Inter-

national Formula, Bulletin Geodesique Organe de la Section

de Geodesie, No. 32, 1931, pp. 327-340.

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as -0.00075.

The change in g from an elevation of 510 meters to an eleva-

tion of 515 meters is given by (18)

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(18) International Critical Tables, v. 1, 1926, p. 402, McGraw-

Hill Book Company, Inc., New York, 370 Seventh Avenue.

-0.0003086 x 5 = -0.00154.

Thus for Ph. v. Jolly's laboratory

$$g = 980.7384 - .00075 - .00154$$

$$g = 980.7361 \text{ cm/sec}^2.$$

To correct the values given in table 6, to 760 mm of Hg,

with g = 980.616, we must multiply by

$$\frac{980.616}{980.7361} = 0.99987754$$

These values are given in table 7.

TABLE 7. - <u>Density of oxygen at 0° C, 760 mm of Hg,
gravity = 980.616 cm/sec^2</u>

	ρ g/l	ρ g/l (Moles 1921)	Ratio
I	1.4289759	1.42885	1.000088
II	1.4290843	1.42895	1.000094
III	1.4289961	1.42887	1.000088
IV	1.4290628	1.42893	1.000093
V	1.4291014	1.42898	1.000085
VI	1.4291372	1.42901	1.000089
VII	1.4290180	1.42886	1.000111
Mean	1.429054 ± 22		

The third column of table 7 gives the values calculated by

Moles (19),

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(19)   Reference 14, page 103.

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decreased by 0.00004, as Moles and **Gonsalez** (20)

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(20)   Reference 15, page 322, Footnote 2.

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indicate should be done.

The fourth column of table 7 gives the ratio of the densi-

ties calculated by me to that calculated by Moles.   The values

differ by almost 100 parts per million (ppm).   This difference

is principally due to the fact that Moles applied a buoyancy

These values are given in table 7.

TABLE 7. - Density of oxygen at 0° C, 760 mm of Hg,
gravity = 980,616 cm/sec²

	ρ g/l	ρ g/l (Moles 1921)	Ratio
I	1.4289759	1.42885	1.000088
II	1.4290843	1.42895	1.000094
III	1.4289561	1.42887	1.000088
IV	1.4290528	1.42893	1.000093
V	1.4291016	1.42898	1.000085
VI	1.4291377	1.42901	1.000088
VII	1.4290780	1.42888	1.000111
Mean	1.4290054 ± 22		

The third column of table 7 gives the values calculated by

Moles (19).

(19) Reference 14, page 101.

decreased by 0.00004, as Moles and Gonzalez (20)

(20) Reference 15, page 122, Footnote 2.

indicate should be done.

The fourth column of table 7 gives the ratio of the densi-
ties calculated by me to that calculated by Moles. The values
differ by almost 100 parts per million (ppm). This difference
is principally due to the fact that Moles applied a buoyancy

correction to the weights in the determination of the mass of oxygen, but he assumed the weights were of brass with a density of 8.4, while I assumed they were platinum with a density of 21.45. This leads to a difference of 87 ppm.

COMPARISON WITH PREVIOUSLY RECALCULATED VALUES OF THE DENSITY OF OXYGEN

In Internal Report No. 44 (21)

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(21)   Barieau, Robert E.

Recalculation of the Work of V. Regnault on the Density of Oxygen. Helium Research Center Internal Report No. 44, November 1963.

I recalculated the work of V. Regnault (22)

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(22)   Regnault, V. Deuxiene Memoire. Sur la Determination de la Densite des gaz, pp. 121-150. Troisieme Memoire. Determination du Poids d air et de la Densite du Mercure, pp. 151-162. Memories de l' Academie Royal des Sciences de l' Institute de France, v. XXI, 1847.

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on the density of oxygen. The comparison of the density of

oxygen follows:

Author	ρ g/l
Regnault, Paris, 1847	1.429626 ± 22
Jolly, Munich, 1879	1.429054 ± 22

This is the density of oxygen in grams per liter, at 0° C and a pressure of 1 atmosphere, where 1 atmosphere is 760 mm of Hg at 0° C in a gravitational field of 980.616 cm/sec^2 in the Potsdam system.

ρ

oxygen follows:

Author	g/l
Regnault, Paris, 1847	1.429026 ± 27
Jolly, Munich, 1879	1.429054 ± 22

This is the density of oxygen in grams per liter, at $0°$ C

and a pressure of 1 atmosphere, where 1 atmosphere is 760 mm of

Hg at $0°$ C in a gravitational field of 980.616 cm/sec^2 in the

Potsdam system.